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Effect of Aging on Rheology & Particle Size Distribution of Monochlorobenzene-in-Ethylene Glycol (Oil-in-Oil) Emulsions

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The effect of aging on rheology and particle size distribution of monochlorobenzene-in-ethylene glycol (oil-in-oil) emulsions, stabilized with polyoxyethylene sorbitan monooleate, has been determined at 30°. On aging of emulsions, there is an increase in globule size and the particle size distribution also becomes progressively broader. The inhomogeneity of non-aqueous emulsions increases with aging time. The fall in viscosity is controlled by the increase in mean globule size (D_m). D_m exerts the same effect on the viscosity of aged emulsions as on the viscosity of freshly prepared emulsions of the same composition.

IT has been shown earlier[1] that in addition to normal oil-in-water and water-in-oil emulsions, it is possible to prepare a third type of emulsions called oil-in-oil (O/O) emulsions using non-aqueous immiscible liquids as continuous and disperse phases and surfactant as emulsifying agent. Emulsions on aging undergo substantial changes in the degree of dispersion of the discontinuous phase before it separates out in bulk. The accumulated data in the literature suggest the following sequence of events: globule flocculation leading to the formation of aggregates, thinning of the film of continuous phase separating adjacent globules within the aggregates, surmounting of the energy barrier and finally globule coalescence. Thus on aging changes do occur in the particle size distribution and rheological properties of emulsions.

In the present investigation attempts were made to study the effect of aging on rheology and particle size distribution of O/O emulsions prepared with monochlorobenzene and ethylene glycol as non-aqueous phases and polyoxyethylene sorbitan monooleate as emulsifying agent.

Materials and Methods

Monochlorobenzene and ethylene glycol used were of BDH grade whereas polyoxyethylene sorbitan monooleate was of K. Light grade.

Preparation of emulsions — Monochlorobenzene-in-ethylene glycol emulsions were prepared using 2·0% polyoxyethylene sorbitan monooleate (w/v % of emulsion). The volume fractions ranging from 0·1111 to 0·6667 of monochlorobenzene were employed. The heterogeneous mixtures of monochlorobenzene and ethylene glycol containing non-ionic surfactant were emulsified with the help of Braun emulsator for final making of the emulsions. Aging was carried out at room temperature (30°) over several weeks in stoppered bottles.

Analysis of particle size — The particle size distribution of non-aqueous emulsions was determined by photomicrographic method[2], by taking photomicrographs of microscopic slides of emulsions on ORWO, NP 27, 400 ASA cut films with the help of Carl Zeiss Jena microscope, equipped with a camera, using a 25X projection system and a 40X objective. An exposure time of 0·02 sec was used by adjusting the illumination so that the motion of the suspended emulsion droplets due to Brownian movement was effectively stopped. Three different areas of each sample slide were photographed.

A stage micrometer, with a ruling of 1 mm long and divided into 100 equal parts, was placed on the microscope stage and the camera and microscope adjustments were made exactly the same as they were when the photograph was taken. With the lines of the stage micrometer carefully focused on the ground glass of the camera, the image was measured with an ordinary millimeter scale. The magnification factor was calculated by the following formula[3]:

$$\text{Magnification} = \frac{\text{Distance in the image field}}{\text{Equivalent distance in the object field}}$$

The processed negatives were placed on a milk glass plate illuminated from the bottom and the individual diameters of 400 to 500 droplets were determined by dividing the observed diameter by the magnification factor.

Immediately after the preparation of an emulsion, the mean volume globule diameter (D_m) was determined. Further determinations were made at frequent intervals during the course of aging. D_m was calculated from the relationship[4]:

$$D_m = \left(\frac{n_1D_1^3+n_2D_2^3+\ldots\ldots\ldots+n_xD_x^3}{n_1+n_2+\ldots\ldots\ldots+n_x}\right)^{1/3} = \left(\frac{\Sigma nD^3}{\Sigma n}\right)^{1/3} \quad \ldots(1)$$

where $n_1, n_2 \ldots\ldots n_x$ are the numbers of globules with diameters $D_1, D_2 \ldots\ldots D_x$ respectively.

Viscosity measurements—A Weissenberg rheogoniometer model R. 16 was used for viscosity determinations. A high rate of shear (1467·6 sec^{-1}) was employed. Cone diameter and cone angle were

7·5 cm and 1° 32′ respectively. A constant temperature of 30·0°±0·1° was maintained by means of a water jacket and all samples were left between cone and plate for half an hour to attain this temperature before viscosity measurements were carried out.

At the high rate of shear employed there was a possibility that frictional heating effects might invalidate the result, but calculation showed this effect to be negligible under the conditions employed. A more serious problem was the danger of sample being thrown out from between the cone and plate at the high rate of shear, which would have lowered the shear stress readings. This danger was minimized by ensuring complete concentricity and alignment of the platens and by checking that the shear stress readings were independent of time.

Results and Discussion

Immediately after the preparation of an emulsion with 0·1111 dispersed phase concentration and 2·0% emulsifier concentration, the particle size distribution data of the typical non-aqueous emulsion were recorded. These are shown in Fig. 1. The O/O emulsion contains low percentage of particles <1·0 μm. On aging of emulsions, there is a progressive increase in globule size and since the emulsions are not monodisperse, the globule size distribution also becomes progressively broader.

Size distribution data have been represented by an inhomogeneity factor (I) which is defined as the mean square deviation of the number-distribution curve with respect to the diameter[5].

$$I = \frac{\int_0^\infty (D-D_n)^2 n_1 dl}{\int_0^\infty n_1 dl} \qquad \ldots(2)$$

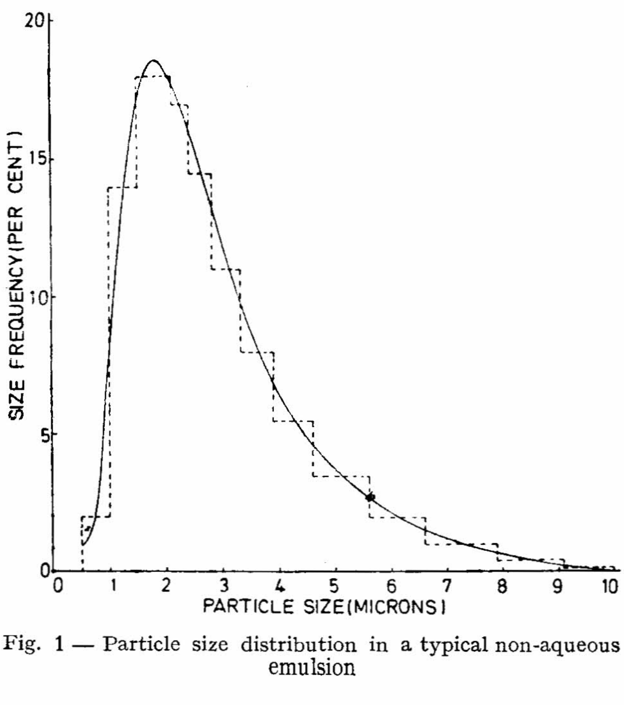

Fig. 1 — Particle size distribution in a typical non-aqueous emulsion

where D is the globule diameter, D_n is the number average diameter ($\Sigma nD/\Sigma n$) and n_1 is the rate of change in the number of particles with their diameter.

On expansion Eq. (2) reduces to Eq. (3)

$$I = a_n/\pi - D_n^2 \qquad \ldots(3)$$

where a_n is the number average area ($\Sigma na/\Sigma n$). The values of I were calculated for all fresh and aged emulsions, and it was observed that I increased with aging time (Fig. 2).

At a high rate of shear, the globules in an emulsion are completely deflocculated and are equidistant from each other. Provided they behave as rigid spheres, this mean diameter of separation (a_m) can be calculated from Eq. (4)[6].

$$a_m = D_m\left\{\left(\frac{\phi_{\max}}{\phi}\right)^{1/3} - 1\right\} \qquad \ldots(4)$$

where $\phi_{\max}$ is the optimum concentration of disperse phase that can be incorporated in the emulsion. In this instance $\phi_{\max}$ corresponds to the theoretical value for equal-sized spheres (0·74) arranged in a hexagonal lattice structure.

By plotting the viscosity data, so as to show the influence of a_m on relative viscosity, η_{rel}, (η_∞/η_0) where η_∞ is the viscosity at high rate of shear such that it is independent of rate of shear and η_0 is the continuous phase viscosity, it is clear that the change in η_{rel} resulting from an increase in a_m is the same for both freshly prepared and aged O/O emulsions (Fig. 3). The progressive increase in D_m is, therefore, due to only aging process exerting a measurable effect on η_{rel}.

From the curves in Fig. 4 showing the effect of aging on η_{rel} of non-aqueous emulsions, it is clear that η_{rel} decreases on aging.

The standard deviations of the results obtained for the measurement of various parameters related to the particle size and viscosity of O/O emulsions were found to be less than 5%.

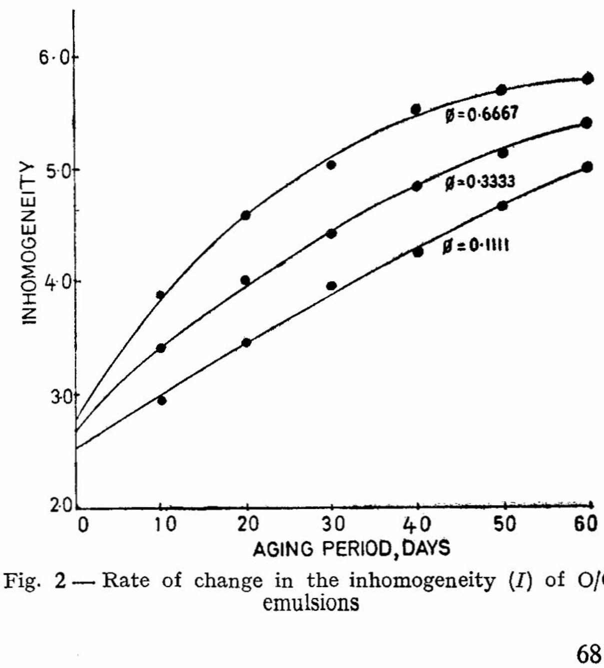

Fig. 2 — Rate of change in the inhomogeneity (I) of O/O emulsions

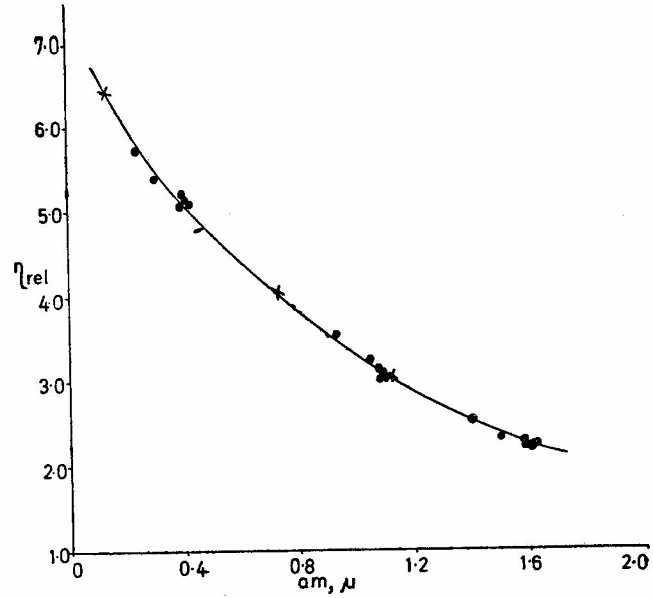

Fig. 3 — The influence of a_m on η_{rel} for aged O/O emulsions [X, freshly prepared emulsions; ⊙, aged emulsions]

Thus it may be concluded that on aging of O/O emulsions, there is a decrease in the number of globules per unit volume of emulsion and an increase in the individual globule size which results in the broadening of globule size distribution. Since it has been established that globule size and size distribution influence emulsion viscosity[7], the latter would be expected to change also when emulsions are aged. In the present study, it has actually been observed that there is a decrease in η_{rel} on

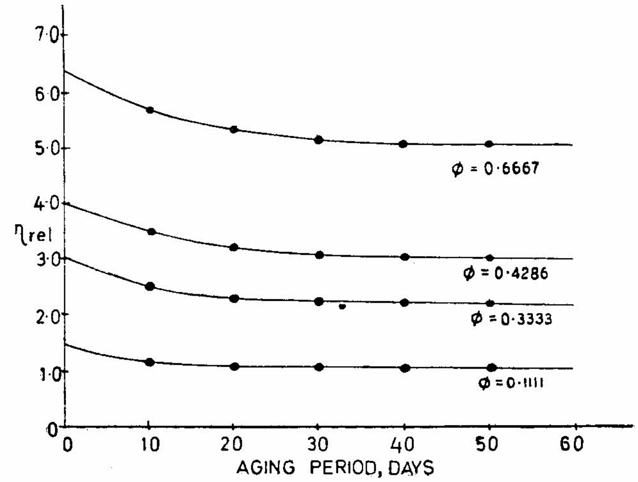

Fig. 4 — Effect of aging on η_{rel} of O/O emulsions

aging of O/O emulsions and the rate of decrease in η_{rel} for the emulsions depends on the rate of increase in D_m.

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